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Low-temperature pyrolysis of wood waste containing urea–formaldehyde resin

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Abstract

A study of the first phase of a thermal two-step process of valorisation for waste containing urea–formaldehyde (UF resins) such as particle boards is presented. The first step of the process known as "purification" is a low-temperature pyrolysis (250–300 °C) achieved for the selective desorption of the additives and their recovery. The second step is a reduction/gasification of the carbonaceous residue by thermochemical attack in CO_2 or in water vapour, to obtain CO/H_2 gases. First experiments have been carried out on a thermobalance to check the feasibility of the selective desorption of UF resin from wood. It appears that the temperature ranges linked to the degradation of wood are different from those obtained for the degradation of urea–formaldehyde resin. Thus, these results enable a selective pyrolysis. Particle board pyrolysis is also studied on an analysis device allowing a semi-continuous analysis by Fourier transform infrared (FTIR) spectrometry of pyrolysis products such as CO, CO_2, CH_4, NH_3 and HNCO. Elementary analysis and studies in calorimetric bomb enable the characterisation of residues after treatment. It appears that the nitrogen quantity eliminated is not influenced by the treatment temperature: the quality of the process does not depend on the temperature of the treatment. However, we also observe an acceleration of the carbon, oxygen and hydrogen elimination, which implies a loss of energy. These results are validated by the study of residues in calorimetric bomb, which leads to an energy loss of approximately 10% for a treatment temperature between 250 and 300 °C.
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Keywords: Wood; Urea–formaldehyde resin; Low pyrolysis; Thermobalance; FTIR

1. Introduction and aim of this study

In the environmental context of the global warming, many alternative solutions have been developed for the production of energy. It is the case for the biomass gasification for heat, electricity or bio-oil generation. Recent works on biomass gasification show that, despite the rise of the oil price, this is a process hardly profitable because of the price of the combustible matter (wood chips), which represents more or less than 50% of the operating costs [1]. The idea is thus to find a lower cost raw matter such as wood waste produced by wood industries, wood frame construction, conditioning or transport. The wood waste containing urea-formaldehyde resin such as particle board constitutes a potential big resource of energy and will induce a negative cost of material. The elimination of this type of waste has become obligatory since January 2002 in order to respect the European legislation, which prohibits the setting in landfill. The presence of some additives in this waste confers to wood a potentially polluting character: UF resin contains a large quantity of nitrogen, which can lead to the formation of ammonia, isocyanic and cyanhydric acid or nitrous oxides during a classical thermal valorisation (combustion or gasification). Therefore, a thermal pre-treatment is needed to "decontaminate" waste before its use as a raw material for gasification.

A two-step process of thermal valorisation can be thus proposed:

- A first step of selective pyrolysis at low temperature (250–300 °C) achieved for the selective desorption of the additives and their recovery. The low temperature allows to limit wood degradation and the level of energy loss and may permit a large lost of nitrogen content.

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- A step of valorisation of the carbonaceous residue by gasification or combustion. For the gasification of the residue by thermochemical attack in CO_2 or in water vapour, we can form a CO/H_2 mix. Moreover, gasification of pyrolysed biomass is often easier to control than classical biomass gasification. A second way is combustion, which allows to recover a large part of the energy contained in the initial waste.

This process enables, on one hand, to eliminate wood waste (which is necessary) and, on the other hand, to produce a cheap raw material, which can be used in a gasification process. We propose to study this process for one of the types of waste that come from wood industry: particle board containing wood and urea–formaldehyde adhesive. The thermal degradation of these various components has already been the subject of various studies in the previous years.

From a kinetic point of view, the biomass pyrolysis has been well studied [2–5] but no model could be clearly established because of the great variability of the resource and because of the operating conditions (temperature, reactional atmosphere, transfer of mass and heat). We can notice however that the temperature range of wood degradation extends from 200 to 500 °C. Between 200 and 280 °C, physical properties of wood change, in the phase known as torrefaction. During this phase, different gases are produced (CO, CO_2, acetic and formic acid, methanol and water), coming mainly from the decomposition of hemicelluloses [1,6–8]. From 280 to 500 °C, the phase of carbonisation takes place where condensable (acid acetic and formic, methanol, tar) and non-condensable (CO, CO_2, H_2, C_xH_y) gases are produced [9]. An exothermic decomposition of cellulose (280–380 °C) is observed followed by endothermic reactions (from 380 to 500 °C): depolymerisations and recombinations within the structure of lignin. The maximum degradation rate is reached between 360 and 370 °C.

The thermal degradation of some types of waste containing wood was largely studied. It is the case for wastes containing CCA [10] or creosote [5,11].

In the case of particle board, waste which contains UF resin, the literature gives only few data.

Studies undertaken by Hirata et al. [12] describe the thermal field relative to the degradation of UF resin. The UF resin pyrolysis is observed between 200 and 300 °C with a maximum in the neighbourhood of 240 °C. During UF resin degradation, we can observe the formation of methanol, ammonia, isocyanic acid, formaldehyde and carbon dioxide [13,14].

We can also find some data in the literature about the formation of N-compounds during reactions of pyrolysis. With regard to the biomass, the work of Tian et al. [15] who studied the formation of the precursors of NO_x during biomass and coal pyrolysis shows that the nitrogen contained in wood or in biomass (from 0.1% to 0.3%) is responsible for the production of ammonia, cyanhydric and isocyanic acid. Hirata et al. [12] worked on UF resin pyrolysis: a weak production of cyanhydric acid starting from 280 °C is observed and becomes much more significant when starting from 350 °C.

2. Experimental

2.1. Sample preparation

Wood, UF resin and particle board samples are provided by a particle board factory. The molar ratio F/U is 1.5/1 for the UF resin. The proportion of wood and UF resin in the particle board is not precisely known. The manufacturer gives us an approximation of the weight percentage (on dry mass) of each component: wood (88–90%), UF resin (10–12%). The particle sizes of samples that have been crushed is lower than 1 mm. The samples were dried in an oven for 4 h at 103 °C before the experiments were performed. Table 1 shows the wood and the particle board elementary analysis realised in the Analysis Central Service of CNRS in France.

2.2. Study on thermobalance

This device (Setaram Setsys 1800) enables to follow the variation of the solid mass (few milligrams) related to temperature and time while controlling the reaction atmosphere. The kinetics of the degradation of wood and of UF resin can be thus studied. The gas flow (nitrogen) is set to 100 ml/min. The weight of samples is close to 150 mg.

We studied the temperature range of wood and UF resin degradation. The temperature of the furnace of the thermobalance was set as follows:

- Gradient temperature from 20 to 130 °C (10 °C/min): phase of drying.
- Isotherm at 130 °C during 30 min: phase of sample weight stabilisation.
- Gradient temperature from 130 to 800 °C (1.5 °C/min): study of the temperature range of wood and UF resin degradation.

These studies allow to specify temperature ranges related to the degradation of wood and UF resin. These tests were thus carried out on samples of wood and of UF resin.

Table 1
Elementary analysis of wood and particle board

	C (wt%)	H (wt%)	O (wt%)	N (wt%)
Wood	50.5	5.9	43.5	0.1
Particle board	47.2	5.8	43.1	5.4

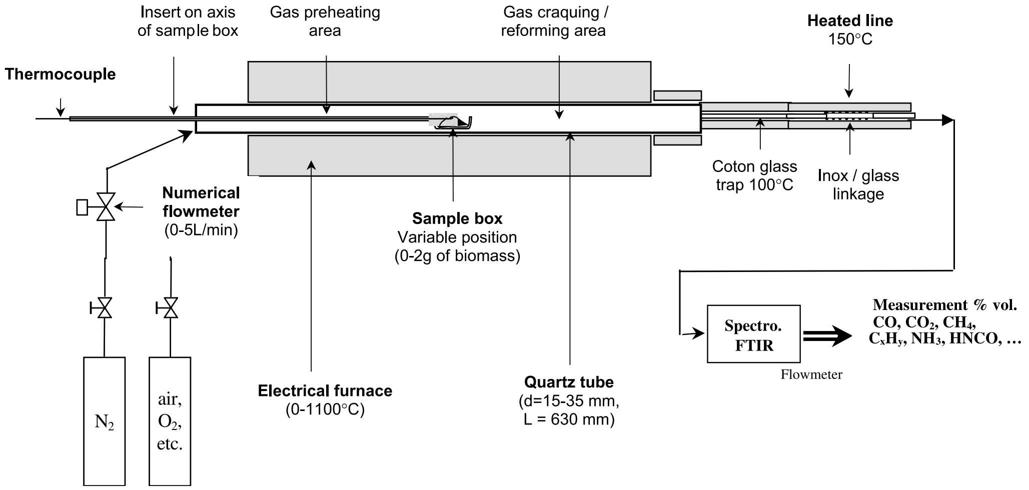

Fig. 1. Sketch of the laboratory study device.

2.3. Study on the laboratory device

The experiment described in Fig. 1 consists of a quartz tubular reactor whose temperature is controlled by a regulated electrical furnace. A quartz sample box enables the insertion of waste (a few grams maximum) in the reactor whose temperature can reach 1200 °C. The experiments can then be carried out in conditions of fast pyrolysis, which is not possible with the thermobalance. An automatic system of insertion allows to choose the introduction velocity and the position of the sample box in the reactor. The device is fed with a gas flow controlled by flowmeters, allowing the introduction of the appropriate gas mixture (nitrogen, air, vapour of water, CO_2). The variation of the position of the sample box, of the gas flow and of the diameter of the tubular reactor allow to control the residence time of the fumes in the device. This experiment thus enables the control of all the parameters of thermal degradation, which are the increasing speed of the temperature of the particles, the final temperature of degradation, the residence time of the pyrolysis products, the grain size of the particles and, finally, the reactional atmosphere. The gases resulting from the selective pyrolysis of waste go through the spectrometer FTIR (Bruker Equinox 55) where their composition is measured. This device enables to follow in a semi-continuous way (time of sampling: 15 s) the evolution of carbon dioxide and monoxide, of light hydrocarbons (methane, ethane, ethylene, etc.), of N-compounds (NO, NO_2, NH_3, HCN, HCNO), of formic and acetic acid and finally of methanol contents. Thus, this device configuration allows analysis of the composition of pyrolysis products except for hydrogen.

Tests are carried out in two steps: the first phase is the determination of the optimum times of treatment according to the treatment temperature and the second consists in specifying the volumes of CO, CO_2, CH_4, NH_3 and HNCO produced during each treatment. The nitrogen flow in the reactor is set at 2 L/min. The temperature of the pyrolysis atmosphere is fixed at the temperature of treatment (250, 260, 270, 280, 290 and 300 °C). A 1 g sample is placed in the sample box. Once the sample has been set up, a short delay is necessary to purge the device in order to realise a correct reference measurement with the FTIR spectrometer. The resolution of the FTIR spectrometer is 2 cm^{-1} and each spectrum corresponds to the average of five scans. The FTIR spectrometer records one spectrum each in 15 s. The gas cell has a volume of 100 ml and is heated to 200 °C to avoid any condensation that would damage the very sensitive windows in KBr (potassium bromide) with water and tar. In order to determine optimum times of treatments, three tests of 20 min are carried out for each temperature of treatment (250, 260, 270, 280, 290 and 300 °C). The 80 spectra recorded are treated by a method of quantification regularly calibrated using standard gas bottles. For HNCO, no gas bottles can be found; therefore, the contents of HNCO in gas product is expressed in percentage of the maximum value obtain during all experiments. The evolution of the content of CO, CO_2, CH_4, NH_3 and HNCO is represented on Excel graphs. Characteristic frequencies of these compounds are reported in Table 2.

Table 2
Characteristic frequencies of the different components found in pyrolysis products

Compound	Frequency (cm^{-1})
H_2O	1300–2000
	3500–4000
CO_2	600–700
	2250–2400
CO	2050–2250
NH_3	800–1100
HNCO	2200–2350

After having determined the durations necessary for each temperature of treatment (set at the time for which the

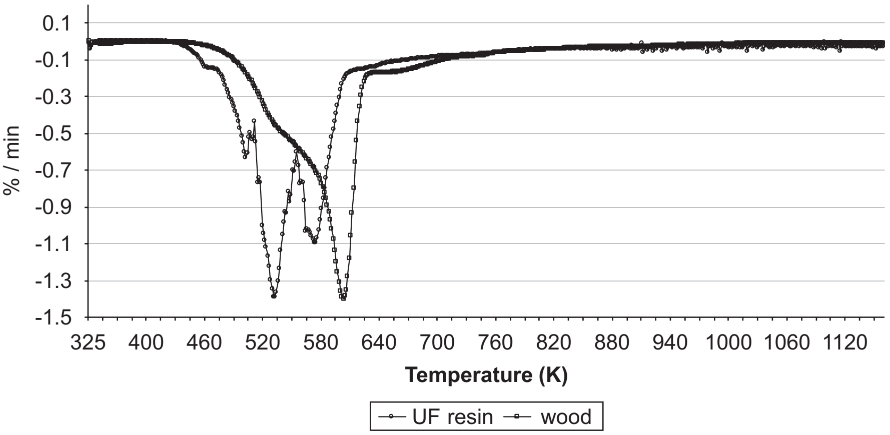

Fig. 2. DTG diagram of wood and UF resin (1.5 °C/min).

level of HNCO reaches a value lower than 3% of the maximum value reached in all tests), the purpose is to measure volumes of CO, CO_2, CH_4 and NH_3 produced during each treatment and to characterise the residues in order to evaluate the accuracy of the treatment. These tests are achieved as previously. For each couple temperature/time of treatment, three tests are carried out. The measurement of the residues weight at the end of each test allows the evaluation of the level of degradation of waste for each couple time/temperature of treatment. The volume volatilised during the treatment for each of these gases is quantified via the integration of the evolution curves of the proportions of CO, CO_2 and NH_3. Performances of the process are evaluated, thanks to an elementary analysis of the residues. From a ‘‘purification’’ point of view, the more the degraded nitrogen level is significant, the more the waste is ‘‘purified’’. From an energy point of view, the lower the degraded carbon and hydrogen levels are, the highest the efficiency is. The low heating value (LHV) of the residues is determined by the study of the residues in a calorimetric bomb.

3. Results and discussion

3.1. Study on the thermobalance

The results obtained for wood are in good agreement with the data of the literature [2,5,6,8]. The temperature range of wood degradation extends from 200 to 500 °C with a maximum around 370 °C (Fig. 2).

For UF resin, we show that the range of temperature of degradation extends from 200 to 300 °C with two maximums at around 240 and 290 °C. These results are in good agreement with those obtained by Hirata et al. [12].

These results highlight the shift between the temperature range of wood and the one for UF resin degradation, which makes possible the selective pyrolysis. Indeed, for temperatures between 250 and 300 °C, the volatilisation of resin should be significant while the one for wood should be limited. As a result, tests were carried out on the study device in this temperature range.

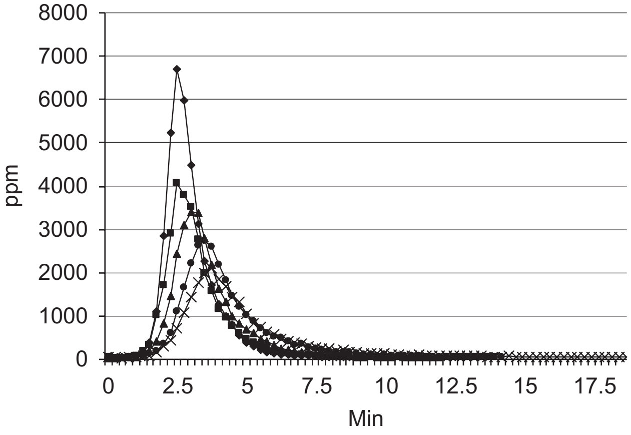

Fig. 3. Evolution of NH_3 level in pyrolysis products during treatment at different temperatures.

3.2. Study on the laboratory device

The breakdown products of the urea–formaldehyde resin at temperatures lower than 350 °C are mainly N-compounds such as isocyanic acid and ammonia [15]. Indeed, the results given by FTIR spectrometer show the presence of these two nitrogenised gases. We can distinguish on the IR spectrum the peaks corresponding to ammonia, isocyanic acid, CO, CO_2 and H_2O. It also appears that hydrocyanic acid is not produced at this temperature.

Thanks to these measures, we can follow the formation of nitrogen during the thermal treatment. The results show that the two main gases containing N during pyrolysis are NH_3 and HNCO. In this way, we obtain the two curves presented in Figs. 3 and 4, which represent the evolution of NH_3 and HNCO content during treatment for the different levels of treatment temperature. NH_3 level is expressed in ppm whereas HNCO level is expressed in percentage of the maximum value achieved in all experiments. The aim of the

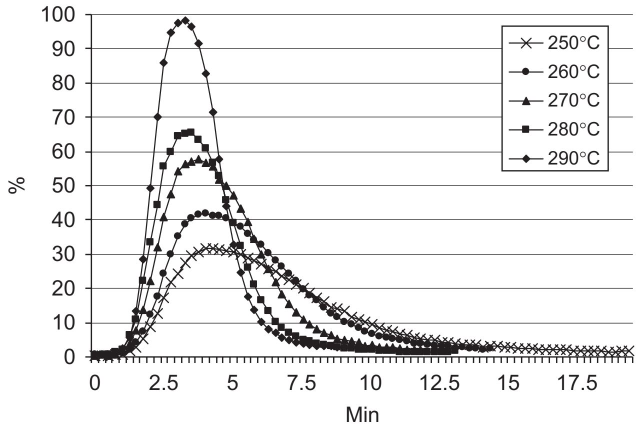

Fig. 4. Evolution of HNCO level in pyrolysis products during treatment at different temperatures.

Table 3
Evolution of the treatment time (min)

T (°C)	NH_3	HNCO
250	11	14.5
260	10.25	13
270	8.25	11
280	7.5	9.5
290	6.25	9
300	5.5	8

treatment is to eliminate nitrogen from waste; therefore, by following the contents of NH_3 and HNCO in gas product, it is possible to qualify the performance of the process. NH_3 and HNCO levels increase quickly in the first minutes of the treatment showing the efficiency of the process. These levels decrease just after to achieve a value close to zero, the treatment is thus inefficient in terms of nitrogen elimination. These results show that the treatment is efficient just during a certain duration depending on the temperature. The aim of this part is thus to determine the optimum duration of the process in a function of the treatment temperature.

Concerning the evolution of ammoniac, the treatment duration is set to the duration necessary for the ammoniac proportion to reach a value lower than 100 ppm. For the evolution of isocyanic level, the treatment duration corresponds to the time when the proportion of HNCO reaches a value lower than 3% of the maximum value reached in all tests. Different treatment durations are reported in Table 3 and show that isocyanic acid stays for a longer time in pyrolysis products. Thus, the optimum treatment duration is obtained from the evolution curves of isocyanic acid level.

After each treatment, the weight of residue is measured in order to determine a degradation level for each couple duration/temperature of the treatment. The evolution of the residual weight percentage with the temperature can be observed in Fig. 5. Although the duration of treatment decreases with the increase of temperature, the degradation level of waste increases with the treatment temperature. Quantities of ammoniac, carbon monoxide and dioxide produced during each treatment are obtained by integrating the evolution curves of the different gas levels in pyrolysis products. Results can be observed in Fig. 6. The humidity of sample is measured by successive weighing after being placed in an oven at 103 °C (humidity is about 6%).

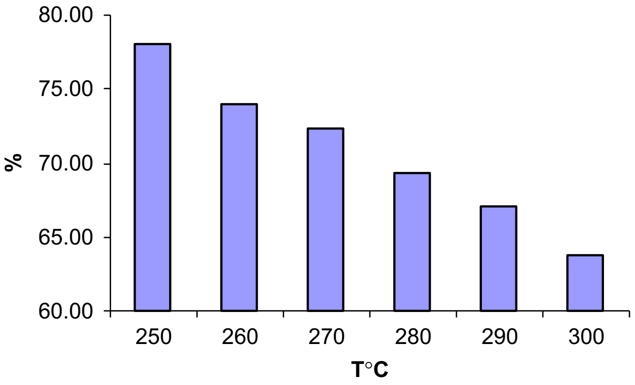

Fig. 5. Evolution of residual weight percentage after treatment at different temperatures of 1 g of particle board.

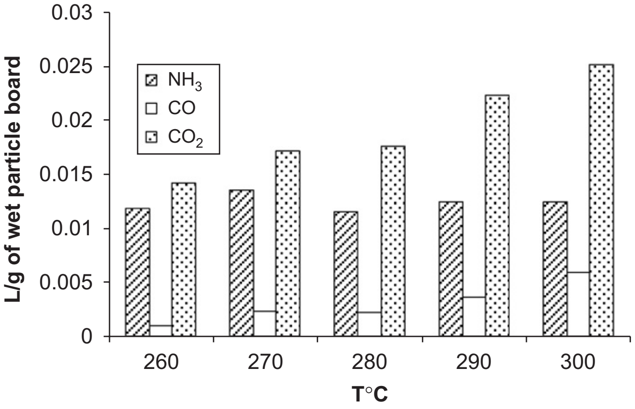

Fig. 6. Curves representing the evolution of the gas volume produced during treatment at different temperatures.

We can observe that the volume of ammoniac produced during the different treatments is relatively constant, contrary to the volumes of carbon monoxide and carbon dioxide, which increase with temperature.

The first results show that the increase of the treatment temperature has no effect on the quantity of ammoniac devolatilised. So, from a ‘‘decontamination’’ point of view, the performance of the process is not influenced by the temperature of the treatment.

The increase of the treatment temperature has however an influence on the quantity of carbon monoxide and carbon dioxide eliminated during the process, and implies a thermal impoverishment of the residue.

Table 4
Elementary analysis of residues obtained after treatment at different temperatures

	C	H	N	O	Residual mass percentage
Particle board non-treated	47.97	6.6	4.29	41.04	100
Particle board treated at 250 °C (14.5 min)	51.32	5.68	2.3	39	78
Particle board treated at 260 °C (13 min)	52.45	5.56	2.71	39.12	74
Particle board treated at 270 °C (11 min)	52.95	5.66	2.25	37.33	72.5
Particle board treated at 280 °C (9.5 min)	52.09	5.39	3.25	38.33	69.5
Particle board treated at 290 °C (9 min)	54.59	5.51	2.46	37.26	67
Particle board treated at 300 °C (8 min)	56.4	5.61	2.15	35.72	63.5

The elementary analysis will allow to compare these values with the quantities of carbon, hydrogen, oxygen and nitrogen eliminated during each treatment.

The measurement of the LHV of the residues will validate our results concerning their energy impoverishment. The results of the elementary analysis are reported in Table 4.

Levels of devolatilisation of different components such as N, C, H and O are established from the results of the elementary analysis and from the knowledge of the level of degradation of the samples for each treatment. Results show that the level of devolatilisation of nitrogen varies between 45% and 66% and that the average is about 58%. These results validated previously show that, from a "decontamination" point of view, the performance of the process is not influenced by the temperature of treatment.

In the same way, the quantities of carbon, oxygen and hydrogen volatilised during the treatment increase with the temperature, which implies a loss of fuel matter and validates as well the previous results.

Thermal analyses of residues in a calorimetric bomb allow to determine the high heating value (HHV) of residues. The LHV is deduced from the HHV value and from the elementary analyses (the yield of hydrogen is requested).

As we can see in Fig. 7, the LHV of residues increases with increasing temperatures of the process. Indeed, the level of carbon increases while that of oxygen decreases with the temperature (results given by elementary analysis), which explains the results obtained.

Two trends can be observed on a thermal point of view: the higher the temperature is, the higher is the level of degradation of the sample but the highest energy the residue contains. The quantity of energy contained in the residue is obtained by multiplying the LHV of the residue by its weight after the treatment. The results are reported in Fig. 8. We can see that the higher the temperature is, the lower is the quantity of energy contained in the residue. This decrease of the quantity of energy remains moderate in the range of the temperatures studied.

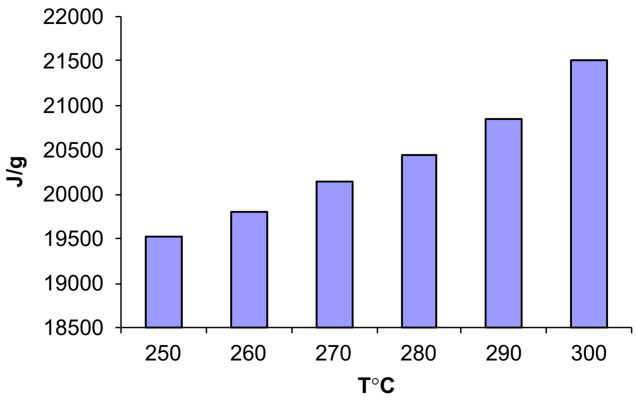

Fig. 7. Evolution of LHV of residues in function of the temperature treatment.

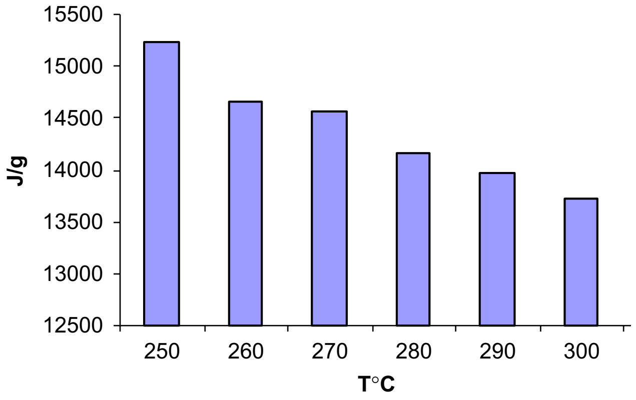

Fig. 8. Evolution of the energy recoverable in 1 g of wet sample in function of the treatment temperature.

4. Conclusions

Thermogravimetric analyses show that the maximum degradation rate of urea–formaldehyde resin and of wood appear at different temperatures (310 °C for the resin against 370 °C for wood), which prove the feasibility of the selective desorption of UF resin from wood waste.

FTIR and elementary analyses show that from a "decontamination" point of view, the performance of the process is not influenced by the treatment temperature.

Thermal efficiency (energy contained in the residue/initial energy contained in waste) decreases with an increasing temperature of the process. The decrease is moderate for temperatures under 300 °C.

A study on an industrial reactor would give an idea of the quantity of energy requested for each treatment and would enable to determine their global thermal efficiency.

The results show the feasibility of the process. Further studies have to be carried out in order to optimise the conditions for the implementation of the two steps.

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